

Ion-Pair Reactivity in Isotopic Exchange Reactions

I. Lithium Chloride in Acetone as Solvent

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Second-order rate constants, k , for the exchange of ^{36}Cl between *p*-nitrobenzyl chloride (*p*-NO₂BzCl) and lithium chloride in anhydrous acetone have been measured at 25° for a range of concentrations of the ionic reactant. The data have been analyzed by means of the Acree equation, $k = k_i\alpha + k_m(1-\alpha)$, where k_i and k_m are rate constants for the reaction of free ions (Cl⁻) and ion-pairs (LiCl), respectively, and α the degree of dissociation of the salt. Values of α were evaluated from ion-pair dissociation constants obtained by means of the Shedlovsky method for different choices of the distance of closest approach of Li⁺ and Cl⁻. The k_m -values found are less than 1 % of k_i indicating that the ion-pairs are kinetically inactive. Assuming k_m to be zero, the dependence of the rate constant, k , on the salt concentration has been employed to calculate the ion-pair dissociation constant. The value 2.83×10^{-6} obtained is to be compared with the dissociation constant 3.39×10^{-6} according to conductivity data.

More than half a century ago it was observed¹ that the specific rate of certain bimolecular substitution reactions involving molecular species, AX, and ionizable reagents, BY, increases with the dilution of the latter. Acree² ascribed this effect to incomplete dissociation of the ionic reactant and a greater reactivity of the ions, Y⁻, compared with the ion-pairs, BY. Using k_i and k_m to denote the rate constants for the reactions of ions and ion-pairs respectively, the observed rate constant, k , may be written,

$$k = k_i\alpha + k_m(1-\alpha) \quad (1)$$

where α is the degree of dissociation of the ionic reactant. Several non-isotopic reactions ($X \neq Y$) have been found^{3,4} to conform to eqn. (1).

A few explicit examples of the applicability of the Acree equation to isotopic exchange reactions ($X=Y$) can be found in the literature. In the following we shall restrict ourselves to this reaction type.

The first test of the Acree hypothesis in the case of isotopic exchange was obviously made by Evans and Sugden,^{5,6} who studied the exchange of bromine

between butyl bromide and lithium bromide in anhydrous acetone. Upon decreasing the salt concentration from 2×10^{-2} M to 5×10^{-5} M, the k -value increased by a factor of nearly 4. However, values of k/α were roughly constant over the whole concentration range studied. According to eqn. (1), this is so if $k_m \ll k_i$ and it was concluded that the exchange takes place primarily through the bromide ions.

The same qualitative conclusion was drawn by Bowers and Sturtevant⁷ in a study of the isotopic exchange between *p*-nitrobenzyl bromide and lithium bromide in an acetone-methanol-water solvent mixture.

Lichtin and Rao⁸ investigated the halogen exchange between *p*-nitrobenzyl bromide and various ionic bromides in liquid sulphur dioxide and found that both ions and ion-pairs are reactive. It was, however, difficult to establish with accuracy the contribution of the ion-pairs to the reaction rate.

The exchange of chlorine between *p*-nitrobenzyl chloride and hydrogen chloride in aqueous dioxane at different temperatures was studied by Bruce, Kahn, and Leary.⁹ The k_m -values reported are approximately 15 % of the corresponding k_i -values indicating that both ions and ion-pairs are reactive in this medium.

It is our intention to make a systematic investigation of the effect of ion-pair formation on the rate of isotopic exchange reactions, especially in systems involving organic and inorganic halides. By employing the comparatively precise electrochemical method¹⁰ to determine reaction rates, we hope that more certain conclusions than before, as to the role of the ion-pairs, may be drawn. In this paper, where data for the isotopic exchange between *p*-nitrobenzyl chloride and lithium chloride in anhydrous acetone are presented, it is shown that the reactivity of the ion-pairs is less than 1 % of the reactivity of free chloride ions.

EXPERIMENTAL

Acetone and *p*-nitrobenzyl chloride were purified and lithium radio-chloride prepared as described in an earlier paper¹¹ in which a detailed account of the kinetic procedure is also given.

Each rate constant quoted below is based upon two analyses of the reaction mixture immediately after mixing the reactants and two further analyses after approximately two half-times of exchange.

KINETIC DATA

A summary of kinetic data, determined at $25.00 \pm 0.02^\circ$ for several lithium chloride concentrations between 1.1×10^{-4} M and 9.6×10^{-4} M, is given in Table 1. The rate of exchange, R , in the next to the last column was calculated using the McKay equation.¹² It has previously been established¹¹ that the reaction investigated is of S_n2 -type and the second-order rate constants in the last column were calculated from the expression, $k = R/[\text{LiCl}][p\text{-NO}_2\text{BzCl}]$.

Table 1. Kinetic data for the exchange of ^{36}Cl between $p\text{-NO}_2\text{BzCl}$ and LiCl in anhydrous acetone at 25.0° .

$[\text{LiCl}] \times 10^4$ M	$[p\text{-NO}_2\text{BzCl}]$ M	$R \times 10^6$ M min $^{-1}$	k M $^{-1}$ min $^{-1}$
9.62	0.04987	6.985	0.1456
5.07	0.04887	4.923	0.1987
3.800	0.0651	5.514	0.2229
3.118	0.04541	3.557	0.2512
3.048	0.0590	4.399	0.2446
2.676	0.0559	3.942	0.2635
2.440	0.03000	2.030	0.2773
2.085	0.03803	2.442	0.3080
1.914	0.04734	2.639	0.2912
1.470	0.03288	1.746	0.3612
1.224	0.04359	2.002	0.3752
1.105	0.02935	1.295	0.3992

ION-PAIR DISSOCIATION CONSTANT

To interpret the kinetic data, the degree of dissociation, α , and hence the dissociation constant, K , of lithium chloride in acetone are required. Recently reported conductivity data¹³ for this salt have been used to evaluate K by means of the Shedlovsky method,¹⁴ which involves the equation,

$$\frac{1}{\Lambda S} = \frac{1}{\Lambda_0} + \frac{c\Lambda S\gamma^2}{K\Lambda_0^2} \quad (2)$$

where,

$$S = \left(\frac{\beta\sqrt{c\Lambda}}{2\Lambda_0^{3/2}} + \sqrt{1 + \frac{\beta^2 c\Lambda}{4\Lambda_0^3}} \right)^2 \quad (3)$$

$$\beta = \frac{8.204 \times 10^5 \Lambda_0}{(\epsilon T)^{3/2}} + \frac{82.5}{\eta\sqrt{\epsilon T}} \quad (4)$$

$$\log \gamma \approx \log f = -\frac{1.8246 \times 10^6 \sqrt{c\alpha}/(\epsilon T)^{3/2}}{1 + 50.29 \times 10^8 \alpha \sqrt{c\alpha}/\sqrt{\epsilon T}} \quad (5)$$

$$\alpha = S\Lambda/\Lambda_0 \quad (6)$$

in which Λ =equivalent conductivity; Λ_0 =limiting equivalent conductivity; c =molar concentration; ϵ =dielectric constant of the solvent; T =absolute temperature; η =viscosity of the solvent; γ =mean molar activity coefficient; f =mean rational activity coefficient; a =distance of closest approach of the ions.

Starting with an approximate Λ_0 , better Λ_0 -values were calculated successively from eqn. (2) by fitting straight lines to values of $1/\Lambda S$ vs. $c\Lambda S\gamma^2$ according to the method of least squares until the difference between successive Λ_0 -values was less than 0.01 %. Finally K was evaluated. The values 20.7

for ϵ and 0.00316 poise for η were used.¹⁵ Bracketed conductivity data in Ref. 13 were omitted because they deviate from linearity in the Shedlovsky plot. The iterations were performed by the aid of an IBM 1620 computer.

To investigate whether the choice of a in the Debye-Hückel equation, the distance of closest approach of the ions, has any significant influence on the result, dissociation constants were evaluated for three different a -values *viz.* 0.0 Å (Debye-Hückel limiting law), 2.41 Å (the sum of the crystallographic radii¹⁶ for Li⁺ and Cl⁻), and 10.0 Å. The results in Table 2 indicate that the ion-pair dissociation constant is very little sensitive to the choice of a .

Table 2. Dependence of K and A_0 for LiCl in acetone at 25° on the a -parameter in the Debye-Hückel equation.

a Å	$K \times 10^6$	A_0
0.00	3.36	213.7
2.41	3.39	212.9
10.0	3.49	210.4

Values of α were calculated for the different dissociation constants quoted in Table 2 by successive approximations from the law of mass action,

$$K = \frac{c\gamma^2\alpha^2}{1-\alpha} \quad (7)$$

and eqn. (5). The result is given in Table 3.

Table 3. Effect of choice of the a -parameter in the Debye-Hückel equation on the degree of dissociation of LiCl in acetone at 25°.

$[\text{LiCl}] \times 10^4$ M	α		
	$a=0.0$ Å	$a=2.41$ Å	$a=10.0$ Å
9.62	0.0612	0.0614	0.0622
5.07	0.0825	0.0824	0.0838
3.800	0.0943	0.0946	0.0958
3.118	0.1033	0.1037	0.1050
3.048	0.1043	0.1047	0.1061
2.676	0.1108	0.1112	0.1126
2.440	0.1156	0.1160	0.1175
2.085	0.1242	0.1246	0.1263
1.914	0.1291	0.1296	0.1313
1.470	0.1455	0.1460	0.1479
1.224	0.1579	0.1586	0.1606
1.105	0.1653	0.1660	0.1681

APPLICATION OF DATA TO THE ACREE EQUATION

To evaluate k_i and k_m , the Acree equation was written in the form,

$$\frac{k}{\alpha} = k_i + k_m \frac{1-\alpha}{\alpha} \quad (8)$$

and a straight line fitted to values of k/α vs. $(1-\alpha)/\alpha$ (Tables 1 and 3) by the method of least squares. The calculations yield the values given in Table 4 indicating that k_i and k_m are not significantly dependent on the choice of the distance of closest approach of the ions in the LiCl ion-pair. The errors attached to k_i and k_m refer to a confidence level of 99 %. The "maximum" k_m -value according to the data in this table, $0.019 \text{ M}^{-1} \text{ min}^{-1}$, amounts to 0.8 % of k_i .

Table 4. Effect of choice of distance of closest approach of Li^+ and Cl^- on k_i and k_m for the reaction studied.

a Å	k_i $\text{M}^{-1} \text{ min}^{-1}$	k_m $\text{M}^{-1} \text{ min}^{-1}$
0.00	2.41 ± 0.18	-0.003 ± 0.021
2.41	2.40 ± 0.19	-0.002 ± 0.021
10.0	2.37 ± 0.18	-0.002 ± 0.021

ION-PAIR DISSOCIATION CONSTANT FROM KINETIC DATA

According to the data above, there is very little evidence for an exchange of chlorine atoms between the lithium chloride ion-pairs and the organic chloride. In fact, the calculated values of k_m in Table 4 are negative, but because of the uncertainty in the determination of this quantity a small positive value, less than 1 % of k_i , cannot be excluded.

We may now reverse the problem and assuming k_m to be zero calculate the ion-pair dissociation constant. In this case the Acree equation is reduced to,

$$k = k_i \alpha \quad (9)$$

which together with eqns. (5) and (7) may be employed to evaluate K .

From eqn. (9) it follows that $\alpha = k/k_i$ and eqns. (7) and (5) may be written,

$$\frac{1}{k} = \frac{1}{k_i} + \frac{c\gamma^2 k}{K k_i^2} \quad (10)$$

and

$$\log \gamma \approx \log f = - \frac{1.8246 \times 10^6 \sqrt{ck/k_i} (\epsilon T)^{3/2}}{1 + 50.29 \times 10^8 a \sqrt{ck/k_i} \sqrt{\epsilon T}} \quad (11)$$

respectively.

A free-hand extrapolation of the rate constants to zero concentration yielded a first, approximate k_i -value, which was used to calculate approximate activity coefficients from eqn. (11) for the actual salt concentrations. A straight line was fitted to the points of $1/k$ vs. $c\gamma^2k$ (eqn. 10) using the method of least squares and a better k_i -value evaluated from the intersection of this line with the $1/k$ -axis. The calculations were repeated until k_i did not change significantly ($<0.01\%$) upon further repetitions. Finally K was evaluated from the slope of the line.

For the concentration range investigated, the relative error in $1/k$ appears to be constant, *i.e.* the absolute error in $1/k$ is proportional to this quantity itself. Therefore, to make the experimental points at high and low $1/k$ -values of equal importance, the straight line according to eqn. (10) was fitted to minimize the sum of the squares of the relative deviations from the line.

This treatment (IBM 1620 computer) of the data in the first and last columns in Table 1, using 2.41 Å for a and 20.7 for ϵ in eqn. (11), yielded 2.83×10^{-6} for K which is in rather good agreement with the dissociation constant 3.39×10^{-6} in Table 2 evaluated from conductivity data.

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